



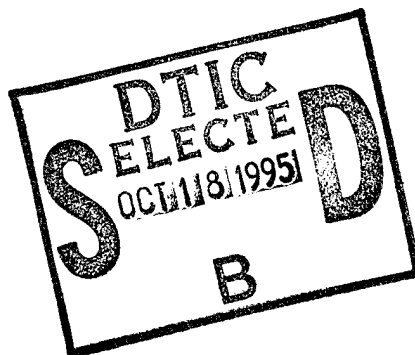
EDGEWOOD

RESEARCH DEVELOPMENT & ENGINEERING CENTER

U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-TR-276

POLYMOLECULAR CLUSTERS: WATER VAPOR'S "HIDDEN PHASE?"



Hugh R. Carlon, U.S. Army Fellow

RESEARCH AND TECHNOLOGY DIRECTORATE

August 1995

Approved for public release; distribution is unlimited.



Aberdeen Proving Ground, MD 21010-5423

19951017 003

DTIC QUALITY INSPECTED 5

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

1995 August

3. REPORT TYPE AND DATES COVERED

Final, 94 Dec - 95 Jul

4. TITLE AND SUBTITLE

Polymolecular Clusters: Water Vapor's "Hidden Phase?"

5. FUNDING NUMBERS

PR-10262622A553

6. AUTHOR(S)

Carlton, Hugh R., U.S. Army Fellow

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

DIR, ERDEC, ATTN: SCBRD-RTE, APG, MD
21010-5423

8. PERFORMING ORGANIZATION
REPORT NUMBER

ERDEC-TR-276

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING / MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Since the early cloud chamber research of C.T.R. Wilson 100 years ago, scientific evidence has existed that water vapor contains huge populations of electrically neutral clusters of water molecules. Hydrogen bonding was unknown to Wilson; therefore, he could not assign a physical basis to these clusters. Thirty years ago, the author began collecting observations and performing new experiments to elucidate the nature of these clusters and their equilibria with their dissociative ions. The experimental results from diverse investigations of atmospheric turbulence, IR absorption and emission, mass spectrometry, vapor electrical conductivity, nucleation events in cooling, saturated water vapor, and moist air are included. The conclusions based on these experimental results are absolutely fundamental to the physical sciences and to our understanding of water itself.

14. SUBJECT TERMS

Water Atmosphere Moist air
Nuclei Nucleation Water vapor
Humidity Water ions (Continued on page 2)

15. NUMBER OF PAGES

28

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION
OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION
OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

UL

14. SUBJECT TERMS (Continued)

IR continuum
 C.T.R. Wilson
 Cloud chamber
 IR absorption
 Water clusters
 Hydrogen bonding
 Neutral clusters
 Water/vapor interface
 Atmospheric turbulence
 Atmospheric electricity
 Electrical conductivity
 CNC (condensation nuclei counter)

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

PREFACE

The work described in this report was authorized under Project No. 10262622A553, CB Defense/General Investigation. This work was started in December 1994 and completed in July 1995.

The use of trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Blank

CONTENTS

INTRODUCTION	7
BACKGROUND	7
FIRST EXPERIMENTATION	8
WATER CLUSTER THEORY	10
MEASUREMENTS OF MASS SPECTRA OF WATER CLUSTERS . . .	16
INFRARED ABSORPTION BY NEUTRAL CLUSTERS IN WATER VAPOR	18
OTHER KINDS OF EXPERIMENTS	21
CONCLUDING REMARKS	26

FIGURES

1.	Equilibrium Curves for Atmospheric Clusters and Aerosols of Many Types at Zero Degrees Centigrade	11
2.	Representation of the Probable Equilibria Associated with the Solid Curve Labeled ION in Figure 1 . . .	13
3.	Some Examples of Possible Structures for Uncharged (Neutral) or Singly-Charged (Ion) Water Clusters .	14
4.	Limiting Numbers of Droplets That Can Be Detected by Condensation Nuclei Counters (or Cloud Chambers) for Saturated Water Vapor at Various Starting Temperatures	15
5.	Mass Spectra for Constant Temperature and Varying Water Vapor Partial Pressure: (a) Spectra at 100 C for Pressures from 42 to 234 Torr (mm Hg); (b) Spectra at 99 C for Pressures from 289 to 417 Torr	17
6.	Emissivity Spectra, Cloud in Moist Air Cooling from 30.5 C to 29.4 C, 71 Observations	19
7.	IR Spectra of Individual Neutral Water Clusters by Size (Ref.17); as Cluster Size (Number of Monomers) Increases from 3 to 6, Cluster Spectra Increasingly Resemble the Liquid Water Spectrum Shown at G . .	22
8.	Schematic Diagram Showing How a Single "Critical" Water Cluster Size of 45 Can Explain All Droplet Nucleation in Water Vapor Over a Wide Range of Temperature and Saturation Ratio	25

POLYMOLECULAR CLUSTERS:

WATER VAPOR'S "HIDDEN PHASE?"

Introduction

I have spent most of my working life with infrared (IR) spectrophotometers, looking through the atmospheric "window" region at 8-13 micrometers (μm) in the IR spectrum. Electro-optical observations and measurements can be made over paths of many kilometers in this window, because normal atmospheric gases do not strongly absorb radiation here. The window is vitally important in the functioning of the "greenhouse effect," which determines the average temperature of the earth's atmosphere, and greatly affects our climate. Sunlight and other visible radiation in the 0.4-0.7 μm portion of the spectrum penetrate our atmosphere and strike the earth's surface. This "hot" radiation causes rapid heating of the surface unless clouds or fogs are present to optically "scatter" the radiation and prevent it from reaching us. We all know how much cooler we feel on cloudy or foggy days, than on sunny ones.

When the earth becomes warmed, it begins to re-radiate into the atmosphere. This re-radiation takes place primarily through the 8-13 μm window. We hear a lot today about "greenhouse gases" which can absorb outgoing radiation even in the window region, trapping heat and contributing to global warming. Carbon dioxide is often thought of like this, when more than normal amounts get into the atmosphere. Many kinds of pollutant gases also are monitored. But I shall try to show in this brief paper how water vapor itself is our most potent, most unrecognized greenhouse gas. Of course, things other than absorption by gases can affect outward IR re-radiation in the 8-13 μm window. In addition to scattering visible light, water clouds and fogs also can scatter, and absorb, IR radiation. But the absorption by water in the IR is far greater than in the visible where, of course, pure water is crystal clear.

Background

I first began to suspect that water vapor contained something really peculiar, some unknown or unrecognized species, about 30 years ago. Since then, I have tried to articulate this fact in many journal publications. But the mere suggestion that something so fundamental could have been overlooked, by everybody for so long, did more to provoke readers (especially if experts in a

field impacted by the new theory), than to stimulate scientific curiosity. Let me take you back to the beginnings of my investigations into whatever is contained in water vapor that makes it so unusual.

Water is well known for its highly unusual thermodynamic properties, which make possible countless phenomena, including life itself. These phenomena are attributable to intermolecular hydrogen bonding that is nearly complete in the liquid phase. To the eye, pure water is a colorless liquid that refracts light and can produce dazzling visual effects, particularly when aerosolized, and brightly illuminated by sunlight. But things are vastly different in the 8-13 μm atmospheric window (Ref.1).

In this IR window, water exhibits enormous differences in spectral absorption between its vapor and liquid phases. At the 10 μm wavelength, the absorption coefficient per molecule of liquid water is 1,000 to 10,000 times larger than this coefficient per molecule of water vapor. (Nonpolar substances that are not hydrogen bonded, on the other hand, have nearly identical molecular absorption coefficients for the vapor or liquid at nearly all wavelengths). A delicate film of liquid water, only 15 μm thick, will absorb half of all IR radiation striking it at the 10 μm wavelength. But water exhibits only small changes in the locations and strengths of its interatomic bands, which help to define the IR window locations, between its vapor and liquid phases. These observations have been accumulated over many years, and they have gradually suggested a fascinating hypothesis: As measured in the 8-13 μm IR window, if water vapor were to contain only 1/10,000 to 1/1,000 parts of liquid-like (hydrogen-bonded) particulate species, its IR absorption would be equal to that of all of the single water molecules (monomers) combined in the vapor. Think of that. And if the particle populations were still larger under certain conditions, they could completely dominate the greenhouse effect, climate, microphysical nucleation mechanisms, and any number of other fundamental phenomena. We are used to thinking of pure water vapor as comprised almost entirely of single water molecules or monomers with perhaps, here and there, an occasional collision-induced water dimer (two monomers, hydrogen bonded for a twinkling of time). How can we argue for, much less justify, such a heretical hypothesis?

First Experimentation

When my colleagues and I first encountered experimental evidence of bogus molecular complexes or "water clusters" in water vapor and moist tropospheric air, we did not have the insights just discussed and so were forced to try to fit our observations to acceptable, professional theories. While developing a long

path IR system, for remote detection of pollutant gases, that operated through the 8-13 μm window, we were troubled by frequent false alarms. These arose because the system scanned analytical and reference wavelengths at a rate of several Hz, and terrestrial scintillations ("heat waves") from the ground had similar rates or frequencies. Thus, if an analytical wavelength were defocused or absorbed, this was interpreted as a detection and the alarm was sounded (Ref.2). We reasoned that if this happened at our site in Maryland, U.S.A., where ground temperatures are moderate and humidities are moderate to high, we should test in Arizona, where desert conditions exist with very low humidities and very high surface temperatures. Extreme, intense terrestrial scintillations as seen in the visible region by the eye, are legendary under these conditions. Yet we observed virtually no scintillation activity in the IR window, and no false alarms in Arizona.

We noted that Tatarski (Ref.3), in his classical treatment of scintillation and wave propagation in a turbulent medium, had completely ignored humidity in the vapor phase. Later, it would become well-known that humidity greatly affects turbulence and IR propagation. But for the time, we could only report that terrestrial scintillation intensity increases with increasing relative humidity. We tried to explain this (Ref.2), by offering two new theories. The first, based upon air refractive explanations, was shown to be incorrect. The second came surprisingly close to the true state of things as we view them now. We proposed that the intense IR turbulence we measured could be explained by relative humidity gradients caused by instantaneous temperature and pressure gradients within the microstructure of heated air. This could lead to the instantaneous formation of tiny "droplets" at the interfaces of air packets or "striae," and the absorption of these water species in the IR could account for the intense beam modulation there. This also explained why our instrument was so much more unstable in humid Maryland, than in arid Arizona, despite the enormous ground-to-air temperatures driving turbulence in the latter desert location.

But what was the physical basis for these "water aerosols" of "sub-micron radius" which were claimed to be present, or to be generated, at higher relative humidities? It was clear that the "aerosols" or species had to be sub-micron in size, because if they were not extremely tiny, they would be easily observed in the visible wavelengths where they would scatter much more light than they could scatter in the IR. Thus the new paradox; how could these "new" species be explained in light of existing cloud physics theory, which holds that all water droplets or aerosols must form on condensation nuclei of some kind?. Later, I collected and published many more examples of very peculiar behavior by water vapor in the atmosphere (Ref.4), and even some examples of how these phenomena might be put to useful applications (Ref.5). Eventually, applications were found and are still in evidence today.

Water Cluster Theory

I began my study of cloud physics with much trepidation and with help from the scientist who began it all-C.T.R. Wilson(Ref.6). A century ago, Wilson carried out early observations of the effects of radiation on water vapor. He showed that X-radiation produced hydrated ions in water vapor that are similar to, but much more populous, than those always found in water vapor that are produced by natural processes. This caused me to note, for later use, that we might use a source like tritium foil to enhance ion formation in water vapor and thus to study the effects of temperature and humidity upon water cluster ions by using a mass spectrometer (this turned out to be extremely fruitful, as will be discussed presently- see Ref.7, which also contains many very pertinent references). It was at first assumed that water clusters formed on ions, but later it was seen that neutral (uncharged), hydrogen-bonded clusters could just as readily become ionized, i.e., that an equilibrium exists between charged and uncharged clusters in water vapor which depends upon parameters including temperature and humidity. The neutrals vastly outnumber the ions, and thus the neutrals are far more important than the ions in phenomena, for example IR absorption, that we'll discuss later. My critics have often failed to make this distinction, ruling out the ions, and thus water clusters in general, as the cause of certain important phenomena. This oversight has fatally flawed many critical arguments against the work discussed here.

Figure 1 shows equilibrium curves for atmospheric clusters and aerosols of many types at zero degrees Centigrade (0 C). Note that as nuclei become smaller (to the left of Figure 1), higher saturation ratios are needed to nucleate a droplet that can then grow (given enough water vapor) to reach visible size for detection. It is very important to note that when one sees a droplet in the vapor, that has grown through orders of magnitude in radius (and through the cube of radius in volume and mass), he can only begin to guess at how it got there in the first place. Cloud chambers give only "end points" for droplets, vastly removed from the nucleation events that produced them, except in the most obvious cases such as for water condensing upon maritime, combustion, or even Aitken nuclei. The solid curve in Figure 1 represents hydrated ions as just discussed here. This is the realm investigated by C.T.R. Wilson, and we recognize also that it is the realm of our "hidden phase" of tiny water "aerosols" or clusters that are necessary to explain the experimental investigations already discussed (and many more yet to come.) The clusters exist in the vapor phase simply because not enough "supersaturation" is available to drive them over the peak of the "ion" curve, thus letting them grow into visible droplets. The clusters can be initially formed about ions, which have a "binding energy" on the order of 1.0 eV but, once formed, a cluster of several water molecules is criss-crossed by a

WATER CLUSTER AND DROPLET EQUILIBRIA

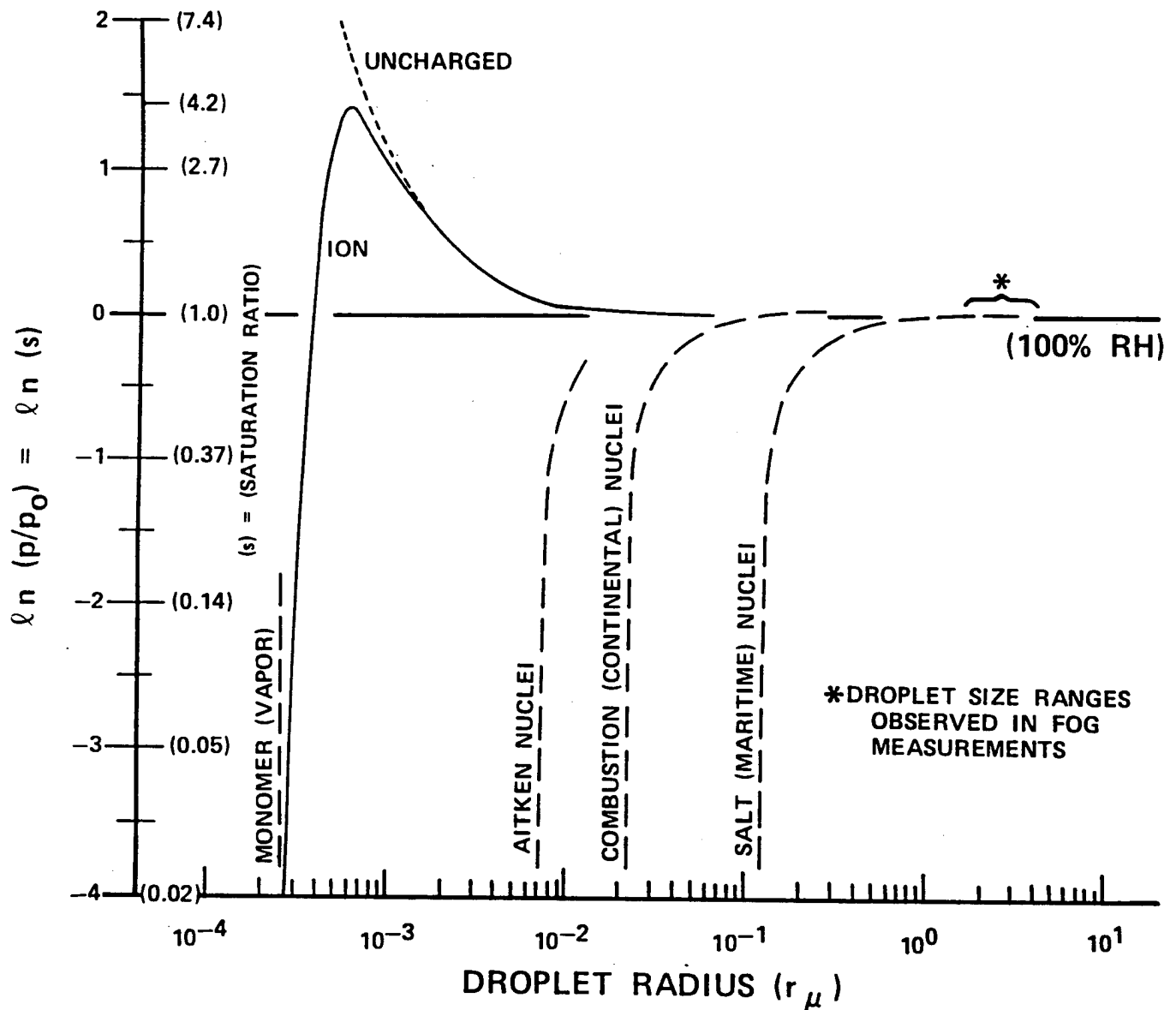


Figure 1. Equilibrium Curves for Atmospheric Clusters and Aerosols of Many Types at Zero Degrees Centigrade.

network of hydrogen bonds, each with a binding energy of perhaps 0.12 eV. A neutral (uncharged) cluster thus can be held together with the energetics of a singly-charged ion one, and there is no reason why they cannot exist together, in equilibrium, for relatively long lifetimes; perhaps, even indefinitely. In this way vast populations of clusters could "store" the water vapor present, without ever growing to critical size for nucleation- and thus giving away their presence by nucleating droplets visible to an observer.

C.T.R. Wilson knew nothing of hydrogen bonding; it would not be discovered for several more decades. And so we have the opportunity to discuss here (1) why he could not fully explain his observations, however brilliant, and (2) how we can now incorporate all of these observations into an extremely useful new theory of cloud microphysics and molecular structure in water vapor, leading to further new directions in classical physics.

The dashed curve labeled "uncharged" in Figure 1 represents Wilson's view of uncharged clusters which were the nuclei for the "cloudlike" condensation in his chambers, as compared to the fewer, larger droplets in his "rainlike" condensation about ions. He simply did not understand what the cloudlike nuclei could be, except collisional dimers or perhaps trimers. Yet the nuclei had average sizes of perhaps 25 monomers clustered together. This led him to suggest that the known radius of the water molecule might be in error by a factor of three! (Ref.7). Instead, the likely state of things at the left end of Figure 1 is shown in Figure 2. There are really two peaked curves rather than one, but they are closely spaced. The upper peak represents huge populations of neutral clusters, possibly ion-induced, responsible for Wilson's cloudlike condensation comprising huge numbers of smallish droplets. The lower peak represents the much smaller populations of water ion clusters, responsible for rainlike condensation. Because there are relatively few ions, the droplets can grow much larger and seem to resemble raindrops. After all, there is only so much water vapor to go around, and there exist upper limits of numbers of water droplets that can be grown and detected in any situation (Ref.8). regardless of the true numbers of nuclei present. This is an extremely important consideration in any argument as to how many neutral clusters can exist in water vapor, and in the atmosphere, at any time. These neutral clusters are the "tiny aerosols" or "hidden species" in water vapor for which our 30-year search was conducted. They can have various sizes and shapes, some of which are suggested in Figure 3. Ion clusters have similar characteristics. Examples of the limiting numbers of detectable droplets for saturated air in a condensation nuclei counter starting over a range of temperatures is shown in Figure 4.

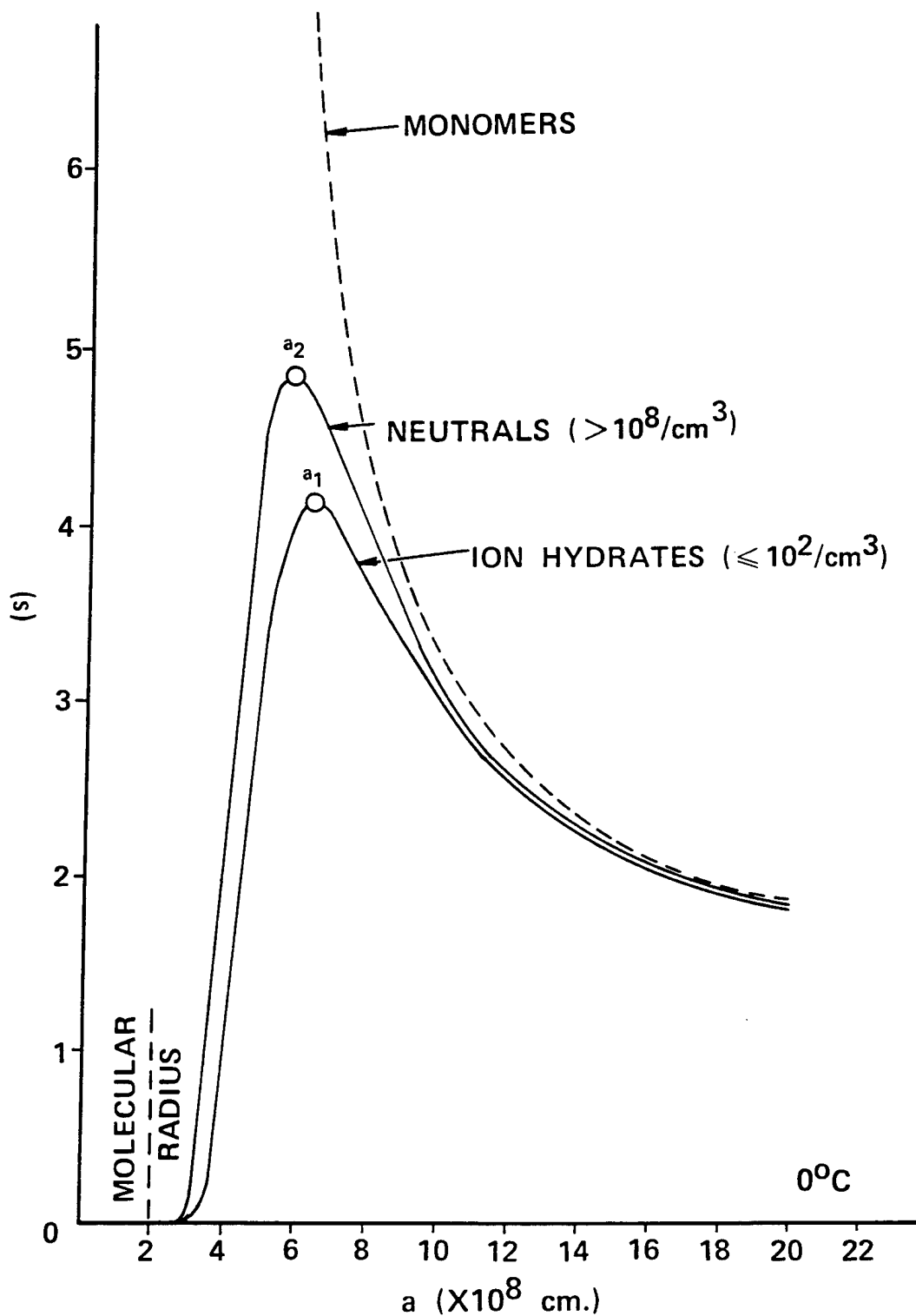
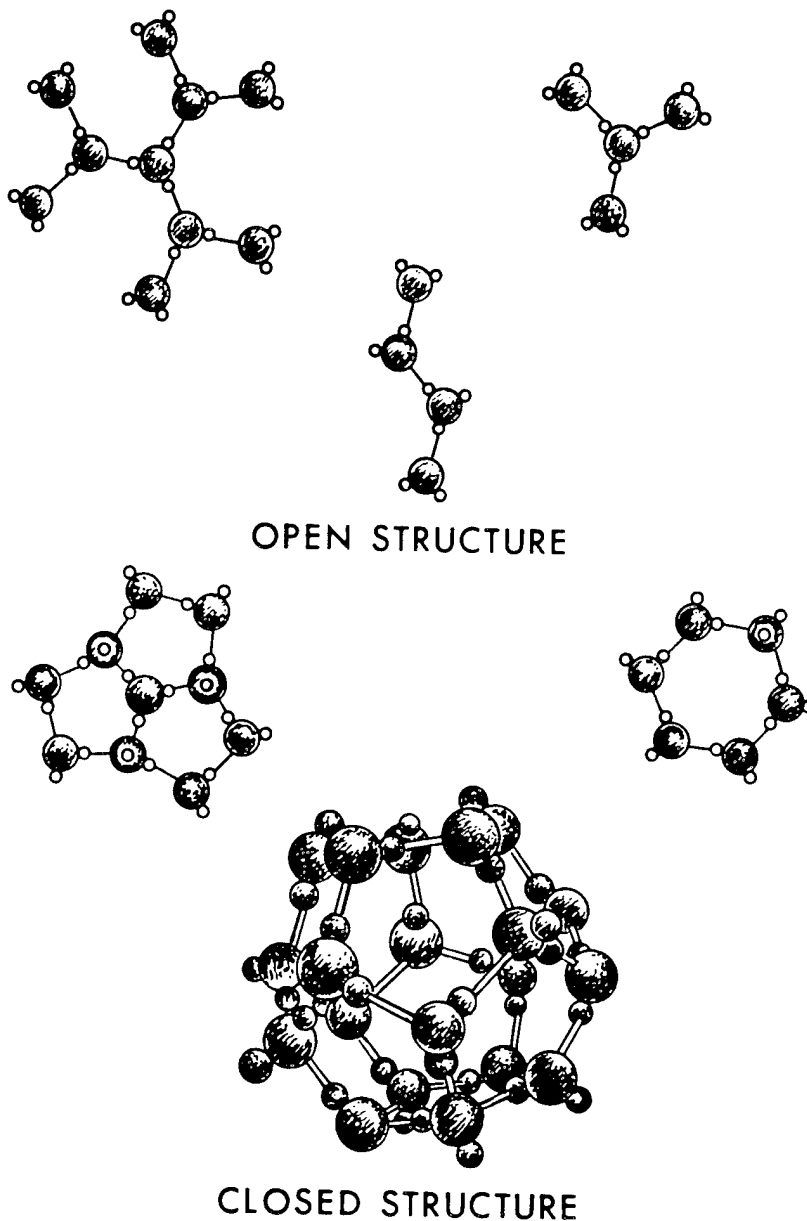


Figure 2. Representation of the Probable Equilibria Associated with the Solid Curve Labeled ION in Figure 1.

EXAMPLES OF WATER CLUSTERS



SOURCE: L.E. STODDARD, J.L. KASSNER

Figure 3. Some Examples of Possible Structures for Uncharged (Neutral) or Singly-Charged (Ion) Water Clusters.

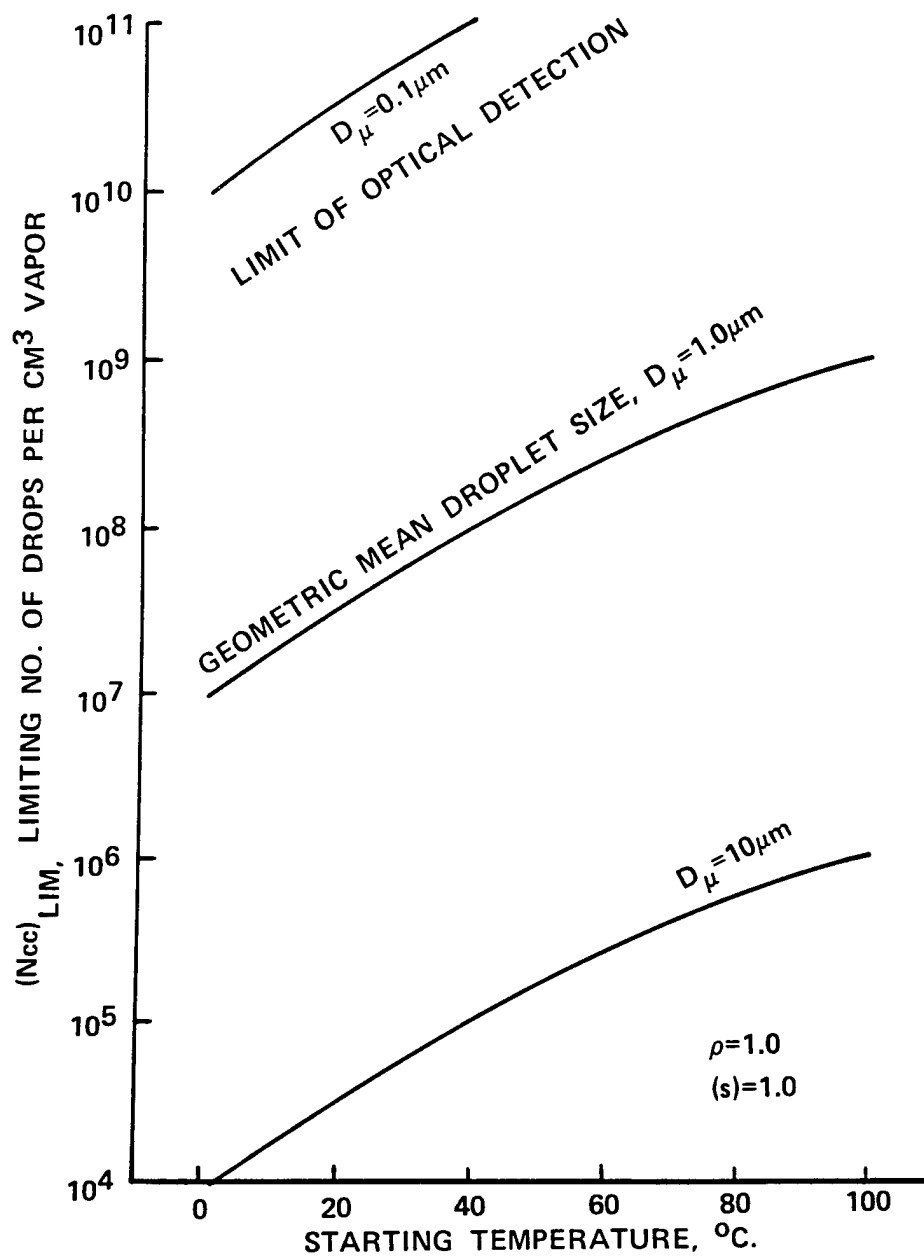


Figure 4. Limiting Numbers of Droplets That Can Be Detected by Condensation Nuclei Counters (or Cloud Chambers) for Saturated Water Vapor at Various Starting Temperatures.

Measurements of Mass Spectra of Water Clusters

A sophisticated mass spectrometer was used to study the water cluster species in moist air near the boiling point for a variety of water vapor partial pressures (Ref.7). An ion source of stainless steel foil coated with titanium tritide with a beta activity of 0.5 Ci was placed at the vapor sampling inlet. The source produced water ions by forming new clusters from monomers and/or by ionizing existing neutral clusters in the vapor by dislodging a single electron. Typical mass spectra produced at a temperature of 99-100 C are shown in Figure 5. Each "spike" represents a water cluster of the "size" or number of molecules (c), ranging from 5 to 45. Very large spikes, like the ones at $c = 21$, reflect very stable, low-energy cluster configurations like the one shown at the bottom of Figure 3. Cluster sizes showing these large spikes are sometimes called "magic numbers."

When we discuss the IR water vapor continuum absorption, which can be convincingly explained by neutral water cluster absorption, we shall learn that this absorption is unique because its intensity has (1) an inverse temperature dependency, and (2) a pressure-squared or quadratic pressure dependency. These can be explained by reference to Figure 5. The beautiful, near-Gaussian cluster size distributions can be conveniently discussed using their mean cluster sizes. At the lowest partial water vapor pressure of 42 Torr (mm Hg), the mean size (c) is only 11-12 molecules. But at $p = 234$ the mean size is near 25, and at $p = 417$ the mean is near 33. The largest cluster for $p = 417$ Torr is 45, and this corresponds to moist air at 99 C and a saturation ratio of only (s) = 0.55, that is, 55% relative humidity. When attempts were made to increase the partial pressure above $p = 417$ Torr, it was found that the right-hand end of the distribution began to "break up." This meant that droplets were being spontaneously nucleated whenever a saturation of 0.55 was exceeded at the boiling point of water. This remarkable result suggested that $c = 45$ could correspond to a "magic number" for a given cluster structure that was the only structure for droplet nucleation, just as water ice has specific structures into which it nucleates and freezes.

The temperature and pressure dependencies of the IR continuum can be explained by cluster distributions. When partial pressure increases, mean cluster size (and also cluster population) increase proportionately. Since absorption of the pure vapor (no clusters) already depends linearly upon partial pressure, the combined effect with sufficient clusters present is a pressure-squared or quadratic dependency. As for temperature (which does not vary in Figure 5), any increase at relatively constant total partial pressure will cause a sharp decrease in relative humidity or saturation ratio. This will immediately shift the cluster size distributions toward smaller values, and also reduce the cluster populations. Both factors reduce the numbers of clustered, liquid-like species

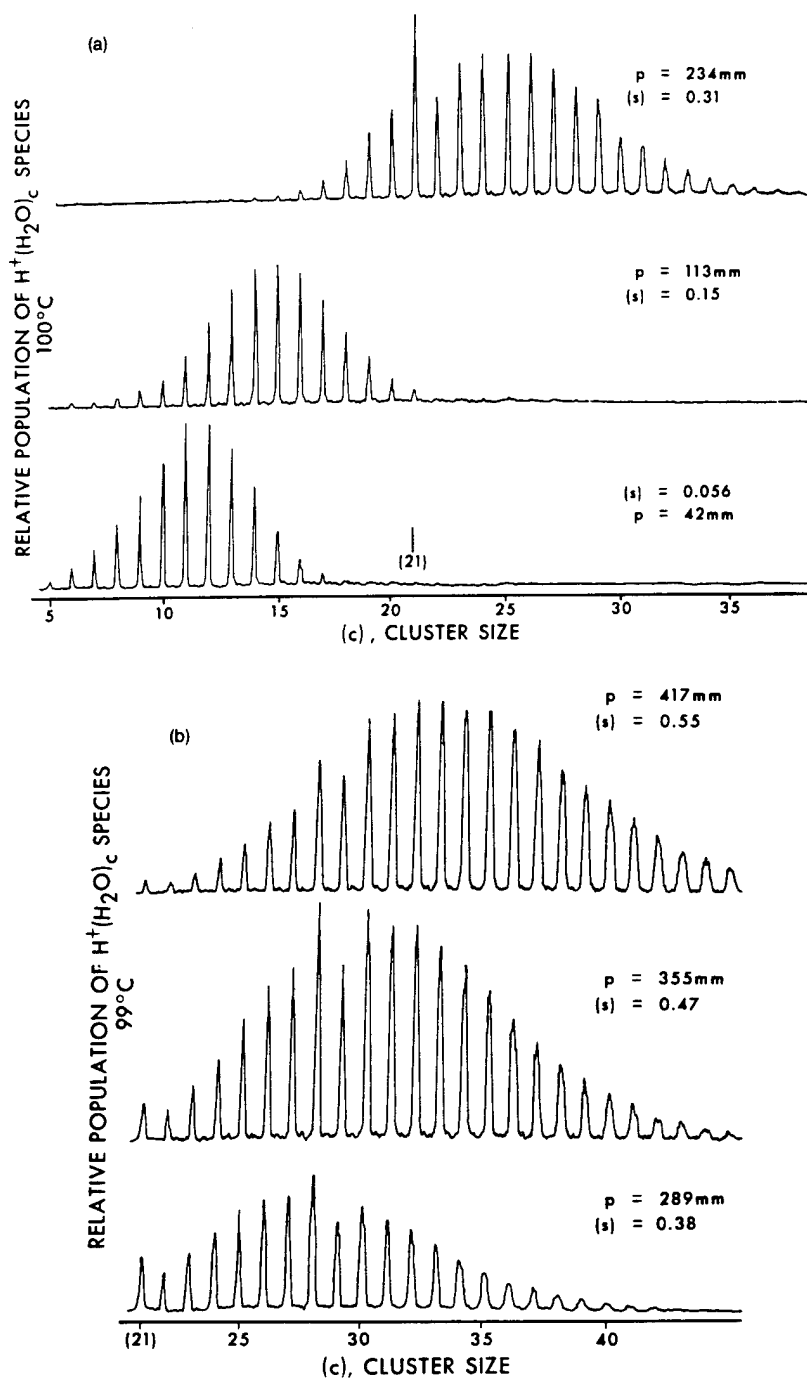


Figure 5. Mass Spectra for Constant Temperature and Varying Water Vapor Partial Pressure: (a) Spectra at 100 C for Pressures from 42 to 234 Torr (mm Hg); (b) Spectra at 99 C for Pressures from 289 to 417 Torr.

present in the vapor, reducing the IR absorption as shown by its inverse temperature dependency. Other clusters, like the dimer, would also produce such dependencies. But their populations, produced by momentary collision and sticking of two monomers, are so tiny as to fall far short of the production of much larger, liquid-like clusters produced in abundance by the mechanisms discussed in this paper.

Our work has shown that there is a direct proportionality between the ion content of water vapor and its neutral cluster content, with the latter being far larger. It has also been shown (Ref.9) that the measured temperature dependency of the IR water vapor continuum absorption is given exactly by the dissociative ion product of pure liquid water, corrected for the partial pressure of water. At face value, this statement appears absurd. But consider that water clusters in the vapor are liquid-like in almost every way, while liquid water is just a collection of clusters. The ion product measures the equilibrium of ions produced from neutral clusters in the liquid, and apparently it does the same in the vapor, with the partial pressure correcting for the huge difference in density of the water phases.

Infrared Absorption by Neutral Clusters in Water Vapor

We have already discussed briefly the water vapor IR continuum absorption (Ref.10), and the early manifestations of clusters in modulating IR absorption in the 8-13 μm window under conditions of severe terrestrial scintillation (Ref.2). But we have made many other kinds of measurements over the years that leave little doubt that evidence for clusters in water vapor is very plentiful. In 1979 (Ref.11) I published results of extremely sensitive measurements of IR emissions from cooling, saturated moist air in a chamber 3 m across. A cryogenic detector was used in an IR radiometer designed with an internal reference blackbody whose temperature could be set to match exactly that of a source blackbody placed opposite the radiometer, both looking through aligned, windowless ports. Lasers provided quantitative measurements of water droplet concentrations in the chamber. Thus, conditions were created such that emitted 8-13 μm IR radiation coming only from the moist air in the chamber was measured as the temperature dropped (maintaining saturation) over a period of about one hour. The results were truly astounding.

Figure 6 shows a typical set of three spectra, taken as the moist air temperature dropped from 30.5 C to 30.0 C to 29.7 C. During this period the droplet mass concentrations in the moist air fell from 4.0 g/cu m to 0.4 g/cu m. The observed spectra went from one (top) with a pronounced "hump" in the middle and effective emissivities greater than 1.0 (indicating an active molecular mechanism taking place in the moist air), through a sudden change

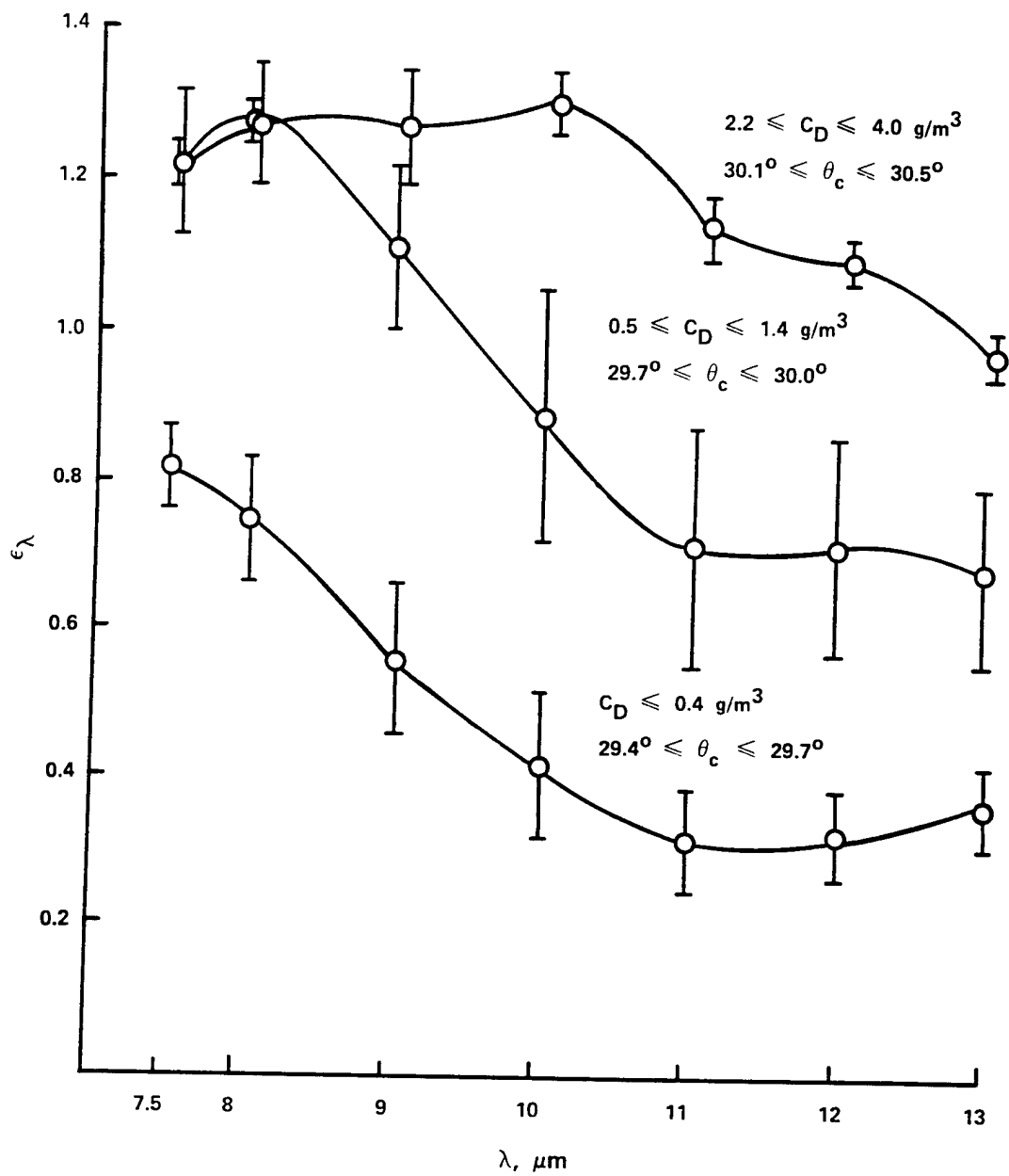


Figure 6. Emissivity Spectra, Cloud in Moist Air Cooling from 30.5 C to 29.4 C, 71 Observations.

in the actual shape of the curve (middle), to yet another shape with emissivities smaller than 1.0. Overall, three kinds of evidence for water species other than the vapor (monomer) and droplets being present in warm, moist air were obtained in repeated experiments:

(1) For lower cloud densities (emissivity less than 1.0), emissions of IR radiation were much larger than could be accounted for by vapor/droplet models; this "excess" emission often abruptly ended when the last droplets evaporated at the end of a trial;

(2) For higher cloud densities (effective emissivity greater than 1.0), emissions were like those noted by other workers who called them examples of "phase transition luminescence" and attributed them to water clusters;

(3) Features ("bumps") in IR spectra were noted like those seen by other workers measuring the IR continuum absorption who concluded that their results were consistent with contributions by hydrogen bonding (clustering) to the IR absorption coefficient of water "vapor."

If distributions of water clusters in the vapor are responsible for the IR continuum absorption and other spectral phenomena, each cluster configuration should have its own individual spectrum. Perhaps populations of a specific cluster kind produced the "bump" in the upper curve of Figure 6. Thus, if cluster distributions are like those in Figure 5, it follows that the broad, small-featured continuum absorption that sweeps across the IR from a few μm to 50 μm should be the envelope of the individual absorption spectra of all clusters comprising the sample. One way to verify this would be to model simple individual clusters to determine their resonant frequencies, and then to use cluster sizes and populations to estimate their contributions to the overall IR continuum absorption. This was first attempted with simple ball-and-spring models (Ref.12).

Even the earliest attempts at calculations of this kind produced absorption spectra that closely matched the shape of the IR continuum. Furthermore, the peak absorption of the entire cluster population occurred near 50 μm , approximating the band shape of the very strong "water rotational band" there. This allows the speculation that this band is not due to rotations of water monomers at all, but to water clusters of myriad sizes, shapes, and populations!

The intensity of the IR continuum absorption can be extremely variable, ranging unexpectedly from non-existent after being taken into account in predictions of atmospheric transmission, to totally dominant under conditions where it has not been considered at all. These are simply manifestations of the activities that produce clusters, and the equilibria that take place between them

when they are present. The vapor-liquid interface is an extremely important area for further investigation. Clearly, clusters must pass through this interface from the almost totally clustered liquid phase to the vapor phase, where individual liquid-like clusters no longer have nearby neighbors but function on their own as tiny, sub-critical, water "droplets" in their "hidden phase." Liquid water's unusual vapor pressure and surface tension are poorly understood. deBoer (Ref.13) has stated that if water behaved as expected from classical theory, the oceans would be dry in a few days. Croxton (Ref.14) states that any statistical mechanical theoretical treatment of the water surface presents very formidable problems and that, indeed, discussion of water's interfacial properties would be "premature." Recent research (Refs.15,16) has shown that evaporation rates from water-wetted materials can be increased tenfold or more by the application of an electric field.

A question of great interest is "how many water molecules does a cluster have to contain before it actually behaves like liquid water?" Fortunately, we know the answer quite precisely thanks to results of clever crossed-beam laser measurements and related thermodynamic studies of clusters (Ref.17). The answer is "the cluster must contain only six or more water molecules". Proof of this is shown in Figure 7 from Ref. 17, showing IR spectra of individual neutral water clusters. The blocks are lettered A. through H., for various samples; liquid water is shown at G. A neutral water cluster of size 3 (at A.) is not spectrally very similar to G. A neutral of size 4 has a somewhat smoother spectrum (B.), and the features at C. begin to round for a pentamer of size 5. At D. the spectrum for a hexamer (size 6), the largest neutral cluster shown here, truly begins to approximate the envelope of the liquid water spectrum at G. These IR spectra were taken at 2-3 um, but in the 8-13 um window region the same clusters also would absorb just as strongly as tiny liquid water species. Thus we are justified in using the complex refractive indices and optical properties of liquid water to calculate those of water cluster distributions in the IR, since nearly all water clusters contain more than 6 water molecules (see Fig.5). We also know that by size 6 an individual cluster already has thermodynamic properties nearly identical to those of bulk liquid water. Hence their slight thermal ionization, following the dissociative ion product of liquid water (Ref.9), would seem to make sense, and would lead to the observed ratios of water ion clusters to neutral clusters that C.T.R. Wilson observed, at least under equilibrium conditions.

Other Kinds of Experiments

If neutral and charged (ion) water clusters have populations that are proportional to each other at equilibrium, then it follows that if we could measure the ion population by the electrical con-

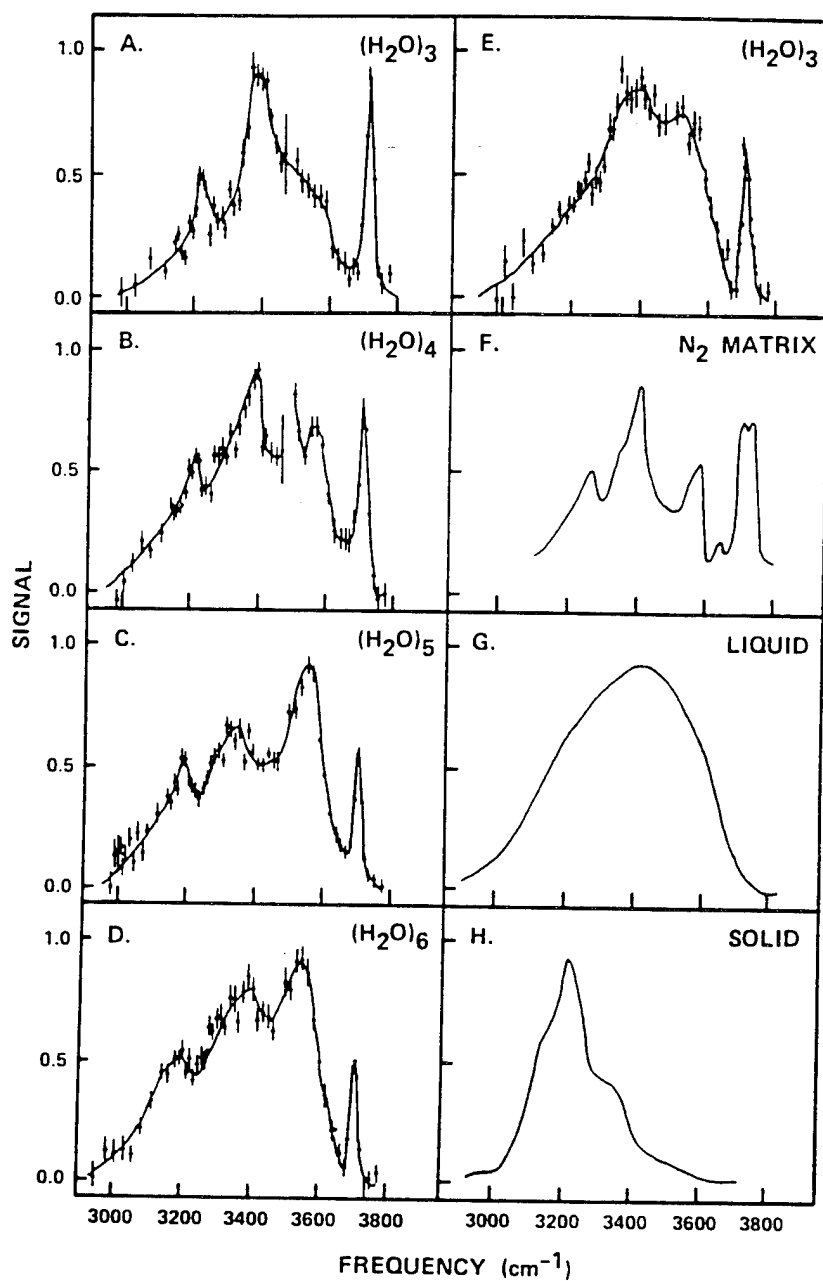


Figure 7. IR Spectra of Individual Neutral Water Clusters by Size (Ref.17); as Cluster Size (Number of Monomers) Increases from 3 to 6, Cluster Spectra Increasingly Resemble the Liquid Water Spectrum Shown at G.

ductivity of water vapor, we could infer much about the vastly larger populations of neutral clusters also present. This would be important because we can not measure directly anything about neutral water clusters floating in the vapor. We can only infer that they are there by measuring excessive IR absorption or emission by the vapor, or by running them through an expansion cloud chamber and observing that droplets can be seen, or by causing them to ionize on the way into a mass spectrometer so their beautiful mass spectra (Fig.5) can be observed responding to temperature, partial pressure, or other parameters. The truth is that there is no definitive experiment yet known that can unequivocally prove the presence of vast populations of neutral water clusters in water vapor. So long as this remains true, it will always be possible for critics from any field of science to "explain" manifestations of water cluster behavior in terms of their own absorption models, or uncertainties of data, or known phenomena that are being misinterpreted, etc. When our minds are made up, we tend to shut out anything new that we don't understand.

I spent many years designing and building precision cells that could be used to measure the electrical conductivity of moist air and, thus, the water ion populations of the air. Since the ion population should be proportional to the neutral cluster population ('tho much smaller), and since the neutrals are strong IR absorbers, one should be able to show, therefore, that the IR absorption of moist air is directly proportional to the ion content of the air. I reported on an ambitious series of experiments of this kind (Ref.18). A folded path optical cell with path lengths of 56.4 and 94.0 m was used to measure IR continuum-like absorption in the 8-13 um window region. Simultaneous measurements were made of the ion content of the moist air, which was humidified by boiling water in a recirculating air flow system. The results showed that the IR absorption was indeed proportional to the ion content of the moist air, and that the observations were consistent with the theory that ions are formed by the dissociation of huge populations of large neutral clusters that are responsible for much of the IR continuum absorption.

There are other regions of the spectrum where, like in the 8-13 um window, water clusters can produce strong absorption and modulation in normally clear window regions. Workers in the microwaves have observed such behavior (Ref.19), which they call "excessive" absorption. A study determined that the absorption in both spectral regions could be explained by the clustering of only about 1/1,000 of the water vapor monomers present, and that the same cluster species probably accounted for observations in both regions. The presence of fog increased the spectral activity, suggesting that evaporation of droplets is a fruitful source of neutral water clusters. Within the fogs themselves, calculations indicated that as much as 1/10 or more of the vapor monomers might be involved in clustering. Often, measurements of electrical con-

ductivity in moist air humidified by steam or ultrasonic atomizers show water ion populations of 100,000 per cu cm or more, about 1,000 times larger than under normal atmospheric conditions. This would indicate that neutral cluster populations under such conditions could involve more than 1/10 of all available water vapor monomers. At the boiling point of water (Fig.5), in closed containers, data often suggest that all water present is involved in clustering to some extent, and that with such enormous vapor/liquid interfacial areas available, a continuum of clustering is approached wherein the remaining vapor, the clustered vapor or "hidden phase," and the liquid itself have very similar characteristics.

I shall now briefly discuss one final set of unusual experiments that were designed to find a scheme of analysis to bring together the many, very different kinds of evidence for clusters that have been discussed in this paper. (Ref.20) evolved from my observation that steaming (droplet formation) above the surface of liquid water that is being heated can first be observed at a temperature of about 50 C under normal atmospheric conditions. Previous observers always presumed that such droplets formed on condensation nuclei always present due to impurities in atmospheric air. But simple experiments, reported in Ref.20, showed that droplet nucleation apparently can occur spontaneously with warming, beginning near 50 C, even in purified saturated air that is free of nuclei other than water clusters. My observations suggested new ideas about structure in water vapor. A cluster size of about 45 can explain observations over a wide range of temperatures and water vapor partial pressures. Note that in Fig.5, no clusters greater than size 45 could be observed and that the clusters begin to "break up" (nucleate droplets) as this apparently critical size for nucleation was approached. It is likely that the shapes of the cluster distributions to the right of their mean sizes are intimately linked to the nucleation rates of droplets that are detected when they reach visible size.

The research reported in Ref.20 led to the publication there of a graphical method (Figure 8) showing how the dynamics of water clustering could be explained using the experimental data discussed in this short paper. The abscissa in Fig.8 is the saturation ratio (s), while the ordinate (n) is the "cluster fraction," that is, the fraction of all water vapor molecules (monomers) that are bound into clusters at any instant of time for the conditions shown. The value of (n) is seen to exceed 1/100 here. The idea of a single cluster size and configuration that is responsible for all droplet nucleation is extremely appealing and adds great credibility to what is presently an ill-defined, highly empirical art which teaches that critical size changes as conditions do! We now have the means to put cloud microphysics on a solid footing.

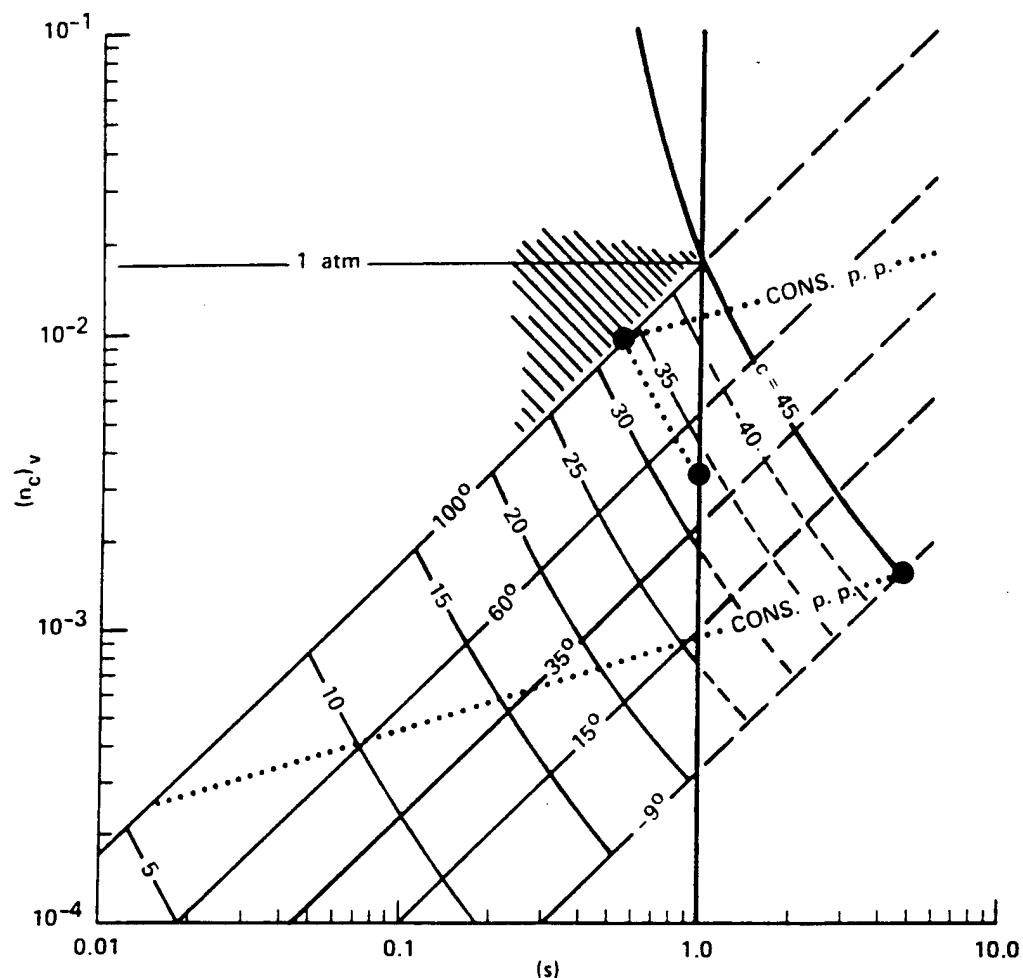


Figure 8. Schematic Diagram Showing How a Single "Critical" Water Cluster Size of 45 Can Explain All Droplet Nucleation in Water Vapor Over a Wide Range of Temperature and Saturation Ratio (See Examples and Details in Ref.20).

Concluding Remarks

The peculiar "hidden phase" which I first realized was present in water vapor 30 years ago, has been identified by combining research in many different disciplines and, with the help of C.T.R. Wilson, observations that leave little doubt as to the true nature of water. The theory is complete. We cannot predict that large populations of water clusters will be in the vapor at any given time or place, any more than we can predict thunderstorms or movements of clouds in the sky days in advance. But when they are present in force, they can show all of the effects that we have mentioned in this paper, and more. Saturation conditions, with droplets present, favor their presence. And under extreme conditions, such as in cooling, saturated steam, cluster activity can be truly astonishing (Ref.11).

One irony in all of this is the part that chance plays in the most fundamental discoveries of mankind. Had Wilson lived more recently, and done his first work in the 1930s or 1940s, the new theories of hydrogen bonding would have been at his fingertips, and he would have understood that huge populations of neutral water clusters of mean size about 25 (Ref.6) were responsible for his "cloudlike" condensation. Moreover, he probably would have understood their equilibria with the far smaller populations of water ion clusters responsible for his "rainlike" condensation. As a further clue, when he tried gases other than moist air in his cloud chambers, he observed that only in hydrogen gas were no ions produced and no "rain-like" condensation produced whatsoever!

He would have pointed to the previously "hidden" cluster phase as a breakthrough in our understanding of water itself, and thus in cloud nucleation and physics, atmospheric electricity, and many other fields. He would have pointed the way to scientists to make great strides in understanding our most basic natural phenomena. But it was not to be. The timing was wrong. Of his "cloudlike" condensation he lamented "it is difficult to account for the immense number of these nuclei....", and we had to wait another 100 years to understand.

REFERENCES

1. H.R. Carlon, "Phase transition changes in the molecular absorption coefficient of water in the infrared: evidence for clusters," *Applied Optics* 17, 3192 (1978).
2. H.R. Carlon, "The apparent dependence of terrestrial scintillation intensity upon atmospheric humidity," *Applied Optics* 4, 1089 (1965).
3. V.I. Tatarski, "Wave propagation in a turbulent medium," translated from the Russian (McGraw-Hill, New York, 1961).
4. H.R. Carlon, "Infrared emission by fine water aerosols and fogs," *Applied Optics* 9, 2000 (1970).
5. H.R. Carlon, "Humidity effects in the 8-13 μ m infrared window," *Applied Optics* 5, 879 (1966).
6. C.T.R. Wilson, "Condensation of water vapour in the presence of dust-free air and other gases," *Philos. Trans. R. Soc. London* 189, 265 (1897) A.
7. H.R. Carlon and C.S. Harden, "Mass spectrometry of ion-induced water clusters: an explanation of the infrared continuum absorption," *Applied Optics* 19, 1776 (1980).
8. H.R. Carlon, "Limits of detection for condensation nuclei counters," *J. Appl. Phys.* 53(9), 6492 (1982).
9. H.R. Carlon, "Infrared water vapor continuum absorption: equilibria of ions and neutral water clusters," *Applied Optics* 20, 1316 (1981).
10. K.J. Bignell, "The water-vapour infra-red continuum," *Quart. J. Roy. Meteorol. Soc.* Vol. 96, 390 (1970).
11. H.R. Carlon, "Variations in emission spectra from warm water fogs: evidence for clusters in the vapor phase," *Infrared Physics* 19, 49 (1979).
12. H.R. Carlon, "Do clusters contribute to the infrared absorption spectrum of water vapor?," *Infrared Physics* 19, 549 (1979).
13. J.H. deBoer, "The dynamical character of adsorption," (Oxford Press, Clarendon, England, 1953).
14. C.A. Croxton, "Statistical mechanics of the liquid surface," (Wiley Interscience, New York, 1980).

15. H.R. Carlon and J. Latham, "Enhanced drying rates of wetted materials in electric fields," J. Atmos. Terres. Phys. 54, 117 (1992).
16. H.R. Carlon and J. Latham, "Accelerated drying of water-wetted materials in electric fields," J. Atmos. Terres. Phys. 56, 487 (1994).
17. M.F. Vernon, D.J. Krajnovich, H.S. Kwok, J.M. Lisy, Y.R. Shen and Y.T. Lee, Infrared vibrational predissociation spectroscopy of water clusters by the crossed laser-molecular beam technique," J. Chem. Phys. 77(1), 47 (1982).
18. H.R. Carlon, "Infrared absorption and ion content of moist atmospheric air," Infrared Physics 22, 43 (1982).
19. H.R. Carlon, "Excessive absorption by atmospheric water vapor in the infrared and 5-17 /cm regions," J. Atmos. Terres. Phys. 44, 19 (1982).
20. H.R. Carlon, "Spontaneous droplet nucleation in clean, saturated moist air at atmospheric pressure," J. Phys. D: Appl. Phys., 17, 1221 (1984).